

## CLAIMS

1. A thermoelectric conversion material having a crystal structure in which a added element or a combination of added elements is or are contained in an amount of 0.001 to 30 at% in silicon, and at least one type of added element is deposited on crystal grains in which silicon accounts for at least 80 at% of the polycrystal structure, and at the grain boundary thereof.
2. A thermoelectric conversion material having a crystal structure in which a dopant or a combination of dopants that generate carriers is or are contained in an amount of 0.001 to 20 at% in silicon, and at least one type of added element is deposited on crystal grains in which silicon accounts for at least 80 at% of the polycrystal structure, and at the grain boundary thereof.
3. A thermoelectric conversion material having a crystal structure in which a dopant or a combination of dopants that generate carriers is or are contained in an amount of 0.001 to 20 at% and a added element or a combination of added elements that do not generate carriers is or are contained in an amount of 0.1 to 10 at% in silicon, and at least one type of added element is deposited on crystal grains in which silicon accounts for at least 80 at% of the polycrystal structure, and at the grain boundary thereof.

4. A thermoelectric conversion material having a crystal structure in which a added element or a combination of added elements that do not generate carriers is or are contained in an amount of 0.1 to 20 at% and a dopant or a combination of dopants that do generate carriers is or are contained in an amount of 0.001 to 10 at% in silicon, and at least one type of added element is deposited on crystal grains in which silicon accounts for at least 80 at% of the polycrystal structure, and at the grain boundary thereof.
5. A thermoelectric conversion material having a crystal structure in which a added element or a combination of added elements that do not generate carriers is or are contained in an amount of 0.1 to 10 at% and a dopant or a combination of dopants that do generate carriers is or are contained in an amount of 0.001 to 10 at% in silicon, and at least one type of added element is deposited on crystal grains in which silicon accounts for at least 80 at% of the polycrystal structure, and at the grain boundary thereof.

6. A thermoelectric conversion material having a crystal structure in which a added element or a combination of added elements that do not generate carriers (except for compound semiconductors) is or are contained in an amount of 5 to 10 at%, at least one type of Group III-V compound semiconductor or Group II-VI compound semiconductor is contained in an amount of 1 to 10 at%, and a dopant or a combination of dopants that do generate carriers is or are contained in an amount of 0.001 to 5 at% in silicon, and at least one type of added element is deposited on crystal grains in which silicon accounts for at least 80 at% of the polycrystal structure, and at the grain boundary thereof.

7. <sup>A</sup> The thermoelectric conversion material according to <sup>any one of</sup> Claims 1 to 6, wherein, of the added elements, the one that generates carriers and is used to make a p-type semiconductor (dopant Ap) is one or more types selected from the group consisting of an Ap1 group (Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, B, Al, Ga, In, Tl) and transition metal elements M<sub>1</sub> (Y, Mo, Zr).

8. <sup>A</sup> The thermoelectric conversion material according to <sup>any one of</sup> Claims 1 to 6, wherein, of the added elements, the one that generates carriers and is used to make an n-type semiconductor (dopant An) is one or more types selected from the group consisting of an An1 group (N, P, As, Sb, Bi, O, S, Se, Te), transition metal elements M<sub>2</sub> (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt, Au; where Fe accounts for 10 at% or less), and rare earth elements RE (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu).

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The thermoelectric conversion material according to <sup>any one of</sup> Claims 1, 3, 4, 5, and 6, wherein, of the added elements, the one that does not generate carriers is one or more types selected from the group consisting of Group IV elements other than silicon, Group III-V compound semiconductors, and Group II-VI compound semiconductors.

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The thermoelectric conversion material according to <sup>any one of</sup> Claims 1 ~~to 6~~ <sup>through 9</sup>, wherein the material is an ingot quenched from a melt, a sinter, a heat treated laminate, or a material having a porosity of 5 to 40%.

11. The thermoelectric conversion material according to Claim 10, wherein the material consists of a p-type or n-type semiconductor material whose carrier concentration is  $10^{17}$  to  $10^{21}$  (M/m<sup>3</sup>) and whose thermal conductivity is no more than 50 W/m · K.
12. The thermoelectric conversion material according to Claim 10, wherein the added element that does not generate carriers is germanium, and the carrier concentration in the semiconductor is  $10^{19}$  to  $10^{21}$  (M/m<sup>3</sup>).
13. A method for manufacturing the thermoelectric conversion material according to <sup>any one of</sup> Claims 1 to 6, including a step of cooling a melt such that added elements are contained in silicon, and with which a crystal structure is obtained in which at least one type of added element is deposited on crystal grains in which silicon accounts for at least 80 at% of the polycrystal structure, and at the grain boundary thereof.

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14. The method for manufacturing a thermoelectric conversion material according to Claim 13, wherein the melting is arc melting or high-frequency melting.
15. The method for manufacturing a thermoelectric conversion material according to Claim 13, wherein the melting and cooling are accomplished by CZ method, FZ method, or ZL method.
16. A method for manufacturing the thermoelectric conversion material according to <sup>any one of</sup> Claims 1 to 6, including a step of powderizing a material containing a added element in silicon, and a step of sintering the powder, and with which a crystal structure is obtained in which at least one type of added element is deposited on crystal grains in which silicon accounts for at least 80 at% of the polycrystal structure, and at the grain boundary thereof.
17. A method for manufacturing the thermoelectric conversion material according to <sup>any one of</sup> Claims 1 to 6, including a step of cooling a melt such that added elements are contained in silicon, a step of powderizing the material thus obtained, and a step of sintering the powder, and with which a crystal structure is obtained in which at least one type of added element is deposited on crystal grains in which silicon accounts for at least 80 at% of the polycrystal structure, and at the grain boundary thereof.
18. A method for manufacturing a thermoelectric conversion material according to Claim 17, wherein a powder with an average crystal grain diameter of 1 to 50  $\mu\text{m}$  and an average particle diameter of 3 to 100  $\mu\text{m}$  is sintered.

19. A method for manufacturing the thermoelectric conversion material according to <sup>any one of</sup> Claims 1 to 6, including a step of coating a silicon powder with a added element or embedding the latter in the former, and a step of sintering the silicon powder, and with which a crystal structure is obtained in which at least one type of added element is deposited on crystal grains in which silicon accounts for at least 80 at% of the polycrystal structure, and at the grain boundary thereof.
20. A method for manufacturing a thermoelectric conversion material according to Claim 19, wherein the added element is contained in the silicon powder itself.
21. A method for manufacturing a thermoelectric conversion material according to Claim 19, wherein the coating step is a vapor phase growth process or a discharge plasma treatment.
22. A method for manufacturing a thermoelectric conversion material according to Claim 19, wherein the embedding step is mechanofusion treatment.
23. A method for manufacturing the thermoelectric conversion material according to <sup>any one of 6</sup> Claims 1 to 6, including a step of forming and laminating layers of silicon or including silicon and layers including added elements, either alternately or in the required pattern, and a step of subjecting the laminated area to a heat treatment, and with which a crystal structure is obtained in which at least one type of added element is deposited on crystal grains in which silicon accounts for at least 80 at% of the polycrystal structure, and at the grain boundary thereof.

24. A method for manufacturing the thermoelectric conversion material according to <sup>any one of</sup> Claims 1 to 6, including a step of cooling a melt such that added elements are contained in silicon, a step of powderizing the material thus obtained, and a step of subjecting a powder to hot pressing or discharge plasma sintering to adjust the porosity to between 5 and 40%, and with which a crystal structure is obtained in which at least one type of added element is deposited on crystal grains in which silicon accounts for at least 80 at% of the polycrystal structure, and at the grain boundary thereof.

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